STUDIES ON THE FLOTATION DEPRESSION OF CHALCOPYRITE, GALENA
AND SPHALERITE BY THIOGLYCOLLIC ACID

by

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ABSTRACT

Thioglycollic acid (TGA) was found to exhibit strong depressive action on chalcopyrite, galena and sphalerite samples. This depressive action resembled hydrosulphide in that the contact curve of TGA was very similar to that of sodium sulphide. An adsorption model was proposed based on the experimental observations. The model suggests that TGA molecules adsorb onto sulphide mineral surfaces through either their mercapto groups, or their carboxyl groups, with subsequent multilayer adsorption of TGA onto this chemisorbed layer through hydrogen bonding and oxidative dimer bonding. The TGA molecules adsorbed through the carboxyl group were not responsible for the observed depression: these molecules were easily desorbed by potassium ethyl xanthate. Oxygen was found to enhance the adsorption of TGA onto sulphide mineral surfaces and consequently, to enhance the depressive action. The selective separation of synthetic sulphide mineral mixtures with the use of TGA has met limited success.
ACKNOWLEDGEMENT

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CHAPTER 1
INTRODUCTION

In 1948, Gibbs patented the use of a series of organic compounds as selective sulphide depressants [1]. They were mercapto carboxylic acids, HS-R-COOH, and a similar type, mercapto thiolic acids, HS-R-COSH; where R represented an organic group, preferably a saturated aliphatic group [1]. These depressants were not used until recently. The simplest form of them, thioglycollate (HSCH₂COOH), has been used in Bagdad Copper, Arizona for about five years [2][3]. Noranda Mines Ltd. is also reported to have used this thioglycollate at Boss Mountain [4]. In spite of the success in plant practice, little is known about the depressive mechanisms involved.

1.1 Review of the Literature

1.1.1 Major Sulphide Depressants

Over the years, a few inorganic reagents have been routinely used as sulphide depressants. For example, sulphite and chromate are used for the depression of galena;
sulphite and zinc sulphate for sphalerite and finally, cyanide is used for copper, zinc and iron sulphides [5]. Arsenical Nokes, a mixture of arsenic trioxide and sodium sulphide, and Nokes reagent, phosphorous pentasulphide dissolved in sodium hydroxide, are copper sulphide depressants [6]. Sodium sulphide (or sodium hydrosulphide) is well known to be depressant for all sulphides [5].

In the copper-molybdenum flotation separation circuit, where the thioglycollate has replaced inorganics in some plants, the predominant scheme is to depress the copper sulphides while capitalizing on the ready floatability of molybdenite to effect the separation. Cyanide is usually added to the pulp if the main copper sulphide is chalcopyrite, whereas ferrocyanide is used if chalcocite is the major copper mineral. Some form of sulphide whether as sodium sulphide, hydrosulphide or phosphorous pentasulphide is used when there is a mixture of copper sulphides[4]. Only in a few cases is the separation effected by depressing the molybdenite with various polymers, while allowing copper sulphide to float [7].

### 1.1.2 Depressive Mechanisms of SH⁻ and CN⁻

Hydrosulphide anion, SH⁻, and cyanide anion, CN⁻, are the two main depressive species for sulphide minerals. Sodium sulphide is a well-known sulphide depressant. A contact curve in Fig. 1 shows that its depressive action
increases rapidly with increase in pH. Examination of the
dissociation curve of sodium sulphide (Fig. 2) shows that
SH" is the only active depressive species in sodium sulphide
solution at pH's greater than 9.

In their recent review, Poling and Beattie [9] have
summarized the depressive mechanisms of a range of
depressants for sulphide minerals. They considered that both
SH and CN depressed the sulphide minerals by displacing
the collector coating from the mineral surface. In addition,
cyanide can leach chemically some metal ions from the
mineral surface, and can also form hydrophilic metal cyanide
complexes which remain adsorbed on the surfaces.

In addition to the above chemical aspect of the
depression, an electrochemical model was also proposed.
First, it was noted that the potential of a copper electrode
immersed in cyanide solutions at various pHs mirrored the
bubble-mineral contact curves, which indicated a definite
correlation between the electrode potential and the
prevention of adsorption of xanthate by chalcopyrite [8]. It
was well documented recently that the adsorption of thio
type collectors onto sulphide mineral surfaces is an
electrochemical process involving electron transfer [10].
The addition of reagents which inhibit this electron
transfer will therefore prevent adsorption of collector,
thus depressing the mineral. The majority of the sulphide
depressants, including SH and CN, have been found to be
Contact curves of sodium sulphide, [KEX]=25mg/l. Extracted from reference [8].

Fig. 1 Contact curves of sodium sulphide, [KEX]=25mg/l. Extracted from reference [8].

Dissociation of sodium sulphide, data extracted from reference [8]. Concentration of S\(^{-}\) ignored.

Fig. 2 Dissociation of sodium sulphide, data extracted from reference [8]. Concentration of S\(^{-}\) ignored.
reducing agents [7]. Janetski, Woodburn and Woods [11] have shown that addition of sodium sulphide prevented the formation of dixanthogen on pyrite in an oxygenated xanthate solution and the pyrite was depressed; the actual electrochemical process in the solution was the oxidation of \( \text{SH}^- \) ions and reduction of oxygen. Agar et al [12] working on the depression of chalcopyrite by KCN in an aerated xanthate solution, have found that it was the potential of the solution rather than the level of KCN which determined the flotation recovery of chalcopyrite (see Fig. 3).

1.1.3 Drawbacks of Inorganic Depressants

Almost all of the inorganic depressants mentioned so far are potentially toxic. Table I presents a list of toxicity data, including those of thioglycollate. These data indicate that only sulphide and thioglycollate are relatively non-toxic.* It is understandable that the increasing health and environmental restrictions are limiting the use of the inorganic reagents.

As mentioned before, it has been shown recently that most of the effective depressants for copper sulphides are strongly reducing, particularly sulphide and hydrosulphide [7]. This finding helped in understanding the depressive mechanism since the adsorption of xanthate on sulphide

* Toxicity data on TGA are sparse (see Table I). Since TGA has been used as an active ingredient in cold-wave permanent hair dressings, it can be safely assumed that TGA is relatively non-toxic.
Fig. 3  Relations Between Chalcopyrite Flotation and Redox Potential of the Pulp [12].
Table I  Toxicity Data of Several Sulphide Depressants

(From reference [13] and [14])

<table>
<thead>
<tr>
<th>reagent index</th>
<th>TGA</th>
<th>KCN</th>
<th>Na$_2$S</th>
<th>As$_2$O$_3$</th>
<th>P$_2$S$_5$</th>
<th>Na$_2$CrO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>orl-rat LD$_{50}^*$</td>
<td>250</td>
<td>10</td>
<td>N.A. &amp;</td>
<td>45</td>
<td>389</td>
<td>N.A.</td>
</tr>
<tr>
<td>TLV**</td>
<td>N.A.</td>
<td>5</td>
<td>N.P. &amp;</td>
<td>0.5(As)</td>
<td>1</td>
<td>0.1(CrO$_3$) #</td>
</tr>
<tr>
<td>TLm***</td>
<td>N.A.</td>
<td>0.16##</td>
<td>61##</td>
<td>5.3@</td>
<td>N.A.</td>
<td>300@</td>
</tr>
</tbody>
</table>

* LD$_{50}$: Lethal Dose 50% kill, mg/kg.

** Threshold Limit Value: the concentration of an airborne constituent to which workers may be exposed repeatedly, day by day without adverse effect, mg/m$^3$.

***Medium Tolerance Limit: 50% of the species studied show abnormal behaviour (including death) within the period of study, ppm.

& Not Available.

&& Not Pertinent.

# Possibly cause lung cancer.

## Bluegill, 48 hours.

@ Salmon, 8 days.

@@ Bluegill, 24 hours.
surfaces is considered as an electrochemical process [10]. Studies also revealed that the wasteful consumption of depressants through oxidation in aerated pulp was inevitable. This explained the high consumption of some depressants. In recent years, a few copper-molybdenum separation plants have started using nitrogen in their flotation circuits to minimize the loss of hydrosulphide [15][16].

At this point it becomes clear why thioglycollate, or a derivative, has spurred great interest, thirty years after the discovery of its depressive action. Although thioglycollate is more expensive than inorganic depressants [3], the additional cost required to treat the waste water when cyanide is used, and the higher consumption when sulphide or hydrosulphide is used might justify the use of this organic depressant. Thioglycollate is also readily oxidized, but the oxidized form can still be an effective depressant. It has been reported that the amount required to achieve the same depression was significantly less with thioglycollate than with inorganic depressants [3].

1.1.4 Properties of TGA Molecule

Thioglycollic acid, a derivative of carboxylic acid, contains two reactive groups, a carboxyl group and a mercapto group. It has a melting point of -16.5°C, a boiling point of 123°C (29 mm Hg) and a density of 1.32, and is
soluble in water, alcohol and ether [17].

The carbon atom of the carboxyl group is bonded to three atoms through $\sigma$ bonds in which three sp$^2$-hybridized orbitals are used. The remaining $p$ orbital overlaps with the $p$ orbital of oxygen to form a $\pi$ bond. The carboxyl group is thus planar, and bond angles for the three bonds each approximate 120°. The hydrogen atom bonded to oxygen is easily ionized because of the other highly electronegative oxygen; the ionized carboxyl anion is highly resonance-stabilized and in reality the negative charge is delocalized over the three atom system—the pair of electrons occupying an extended $\pi$ orbital which encompasses both oxygen atoms and the intervening carbon atom. In this situation the two carbon-oxygen bonds become identical, as shown by the following structure:

$$\text{H} - \text{C} - \text{O}$$

This highly electronegative COOH group withdraws electrons from the sulphur of the mercapto group, thus aiding in the ionization of the proton bonded to the sulphur atom. As a result, the chemical reactivity of the mercapto group is enhanced. For example, the ionization constant for HS$^-$ anion to dissociate into H$^+$ and S$^{2-}$ is $2 \times 10^{-15}$ [8], but the dissociation constant for SH group in TGA is of the order of $10^{-11}$ [17]. TGA is also easily oxidized to form a dimer through $\text{-S-S-}$ bonding (HOOCCH$_2$SSCH$_2$COOH), dithiodiglycollic acid (DTGA), as shown by the half-cell reaction:
\[ 2 \text{TGA} = \text{DTGA} + 2 \text{H}^+ + 2 \text{e}^- \quad (1) \]
\[ E^0 = 0.33 \text{V (vs SHE)} \quad [3] \]

The equilibrium dissociation constants at 25°C are 1.2\times10^{-4} to 2.8\times10^{-4} for the carboxyl group and 2.7\times10^{-11} to 7.6\times10^{-10} for the mercapto group [17]. Either carboxyl group or mercapto group or both can participate in chemical reactions.

1.1.5 Depressive Mechanism of Thioglycollate

Only very few papers have so far been published regarding the depressive action of thioglycollate. Nagaraj et al [7] and Agar [4] both showed that thioglycollate was a strong depressant for chalcopyrite and a strong reducing reagent. Raghavan & Unger [3] have carried out a detailed study of the interaction between thioglycollic acid (TGA) and chalccocite. Using a zinc reduction and iodine titration technique, they observed the rapid production of dithiodiglycollic acid in solution upon contact with chalccocite. They postulated a mechanism by which adsorbed TGA reacted with the TGA in solution to form an oxidized disulphide. The reaction is:

\[ \text{TGA}_{\text{ads.}} + \text{TGA}_{\text{aq.}} = \text{DTGA} + 2 \text{e}^- + 2 \text{H}^+ \quad (2) \]

This reaction is first order in terms of the TGA concentration in solution. They believed that the chalccocite surface was completely covered with adsorbed TGA under the
test conditions and that it catalysed the oxidation. They assumed that the amount of adsorbed TGA remained constant, but did not determine how much this amount was nor how it was adsorbed. In addition, when considering the above proposed reaction (2), in order to maintain the same amount of TGA on the surface, one TGA molecule should be adsorbed onto the surface instantaneously upon formation of a DTGA molecule in the solution. This is difficult to believe. It may be that these authors propose a spontaneous kinetic model in which only a single TGA monolayer is adsorbed on the chalcocite surface. Whenever a TGA molecule comes in contact with the surface, it immediately reacts with adjacent TGA in solution to form a DTGA molecule, which then comes off from the surface so that another TGA molecule can take its place. Since Raghavan and Unger [3] also observed that DTGA was an effective depressant, one may wonder how the depression could be achieved if DTGA was so easily desorbed from the surface? They offered no explanation for the depressive mechanism of DTGA.

One possibility which might explain the observed phenomena is that only TGA is responsible for depression and when pure DTGA is added to solution, an electrochemical equilibrium is set up so that a small amount of TGA is formed. If this is the case, the formation of DTGA is a wasteful consumption of TGA and an inert atmosphere then should enhance the depressive action.
1.2 **Objective of This Investigation**

It is seen from the above review that thioglycollate is now used primarily in the separation of copper-molybdenum sulphide ores, and the depressive mechanisms of thioglycollate are far from clear. In view of this, this experimental work was undertaken to:

a. Test the depressive action of thioglycollate on several other sulphides and look for possible schemes to separate them.

b. Study the influence of oxygen on the adsorption of thioglycollate and on its depressive action.

c. Elucidate, to some extent, the mechanisms involved in thioglycollate depression of sulphide minerals.
CHAPTER 2
EXPERIMENTAL

2.1 Material

The minerals tested were chalcopyrite, galena and sphalerite. Hand-size lumps of pure chalcopyrite from Timagami, Ontario, and pure galena from Osavizawa, Japan, were crushed and ground individually. The size fraction of -100+150 mesh was used for these experiments. Pine Point sphalerite concentrate, also -100+150 mesh in size, was available in the department of Mining and Mineral Process Engineering (MMPE) at the University of British Columbia. The surface area of each sample was determined by nitrogen adsorption using a Quantasorb Sorption System.*

Since these sulphide minerals are readily oxidized when exposed to the atmosphere, they were subject to a pretreatment prior to each test to establish clean and identical surfaces. The pretreatment was performed using an elutriator, very similar to the one described by Harris and Finkelstein [18] (see Fig. 4). For chalcopyrite and galena,

* Model QS-2, made by Quantachrome Corporation, 337 Glen Cove Road, Greevale, N.Y., 11548, USA
Fig. 4  Schematic diagram of the elutriator used for the pretreatment of sulphide minerals
this pretreatment procedure was as follows:

a. place 15 grams of the sample into the elutriator.
b. wash with 1000 ml 0.1M deoxygenated hydrochloric acid solution.
c. seal the elutriator and set to rotate end-over-end for 60 minutes at about 3 rpm.
d. wash with 1000 ml deoxygenated distilled water.

The sample was then filtered, dried and stored in a vacuum desiccator. For sphalerite concentrate, additional treatment was carried out to clean the surface. The cleaning procedure was as follows:

a. Place 15 grams of sample into the elutriator.
b. wash with 500 ml 0.1M deoxygenated sodium sulphide solution.
c. seal the elutriator and set to rotate end-over-end overnight (about 15 hours) at about 3 rpm.
d. wash with 500 ml 0.1M deoxygenated sodium sulphide solution again.
e. wash with 1000 ml deoxygenated distilled water.
f. wash with 1000 ml 0.1M deoxygenated hydrochloric acid solution.
g. seal the elutriator and set to rotate for 60 minutes at about 3 rpm.
h. finally, wash with 1000 ml deoxygenated distilled water.
The samples were then filtered and stored in a vacuum desiccator and were taken out just prior to a test run.

It should be pointed out that although the sulphide mineral samples have undergone the above treatment, they cannot be considered as completely free of oxidation products. This is because the surface oxidation of these sulphide minerals happens in a few seconds when they are exposed to the atmosphere.

The mineral samples tested in this experimental work are listed in Table II. Synthetic zinc sulphide (Irtran II material* from Kodak) was also used for some of the IR spectroscopic studies.

High purity potassium ethyl xanthate, which was available in the Department of MMPE, was used throughout as a collector. No impurities could be found in its infrared spectrum. Fisher brand thioglycollic acid with a specified purity of 96.99% was supplied from the Chemistry Department of The University of British Columbia. Commercial ammonium thioglycollate (ATG), which was produced by Argus Chemical Corporation† and contained 60% NH₄TG, was supplied from VW&R.** Technical grade glycollic acid with a purity of 65-67%, was bought from BDH Chemicals. Hydrochloric acid and sodium hydroxide were both used as pH modifiers. All the

*APPENDIX I shows its production and properties
† 633 Court Street, Brooklyn, N.Y., 11231, USA
** VW&R: Van Waters & Rogers Ltd., 9800 Van Horne Way Rmd. Vancouver, B.C., Canada
Table II  Mineral Samples

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Size(mesh)</th>
<th>Assay (%)</th>
<th>S.S.A. (cm²/g)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>-100+150</td>
<td>Cu 25.95</td>
<td>Fe 32.0</td>
<td>Pb 0.08</td>
</tr>
<tr>
<td>Galena</td>
<td>-100+150</td>
<td>Cu 0.16</td>
<td>Fe 0.16</td>
<td>Pb 81.0</td>
</tr>
<tr>
<td>Galena</td>
<td>-150**</td>
<td>Cu 0.16</td>
<td>Fe 0.16</td>
<td>Pb 81.0</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>-100+150</td>
<td>Cu 0.02</td>
<td>Fe 1.5</td>
<td>Pb 0.40</td>
</tr>
</tbody>
</table>

* Specific surface area, determined by nitrogen adsorption.

** Deslimed by elutriation.
other reagents used were of analytical grade.

2.2 Microflotation

2.2.1 Hallimond Tube Flotation

The floatabilities of the single mineral samples, modified by the reagents, were tested in a Hallimond Tube [19]. Two grams of sample were conditioned with 100 ml potassium ethyl xanthate solution for a period of 5 minutes, then a certain amount of the depressant was added. The pH of the pulp was adjusted, and conditioning was continued for a further 5 minutes. The pulp was then transferred to the Hallimond Tube. While being kept well-suspended by a magnetic stirring bar, the pulp was floated in a nitrogen flow of 30 ml/minute for 1 minute. In some of the tests, the conditioning procedure was reversed purposely.

The sphalerite sample was activated by copper prior to conditioning with xanthate. This was achieved by reacting 16 grams of sphalerite with 400 ml $4 \times 10^{-4}$M copper sulphate solution for 15 minutes at its natural pH. By measuring the residual copper concentration, the copper coverage on sphalerite was found to be 0.4 monolayer at this condition. The calculation was carried out on the assumption that each copper atom occupied $1.04 \times 10^{-19}$ m$^2$ of the surface site.
2.2.2 P/S Cell Flotation*

Synthetic mineral mixtures were separated with a 100 ml P/S cell. After a conditioning period as described in the previous section, the mixture was transferred to the P/S cell. The flotation separation was conducted at a nitrogen flow of 30 ml/minute, while the amount of sample and flotation time were specified individually. The amount of each mineral in the product (concentrate and tail) was assayed by atomic absorption spectroscopy in the assay laboratory of the Dept. of MMPE.

This P/S cell was also utilized for single mineral flotation with potential measurements (see Fig. 5a and 5b for the modified cell). Four electrodes were used: a platinum electrode coupled with a saturated calomel electrode to measure the solution redox potential, an oxygen electrode to measure the oxygen concentration in the solution and a combined electrode to monitor the pH value of the solution.

The outputs of the electrodes were recorded simultaneously. Redox potential of the solution was recorded with a Beckman 10 inch recorder. The readings were checked by a constant power source and a Keithley multimeter.† The electrodes were calibrated against standard solutions [21]. Oxygen concentration was measured by YSI Model 54 oxygen

* Partridge/Smith flotation cell, see reference [20].
† Model 171, made by Keithley Instruments Inc., 28775 Aurora Road, Cleveland, Ohio, 44139 USA
Fig. 5a Schematic Diagram of the P/S Cell Equipped with Four Electrodes for the Simultaneous Measurements of pH, Oxygen Concentration and Redox Potential of the Flotation Pulp.

Fig. 5b The Modified P/S Cell at Work.
meter, and recorded by another Beckman 10 inch recorder. The pH value of the solution was measured and recorded by an Electroscan 30 potentiometer. These micro-flotation tests with potential measurement were conducted in both aerated and argon-saturated solutions.

a. In aerated solution.

Two grams of xanthated sample were placed into the P/S cell, 100 ml of 0.001M depressant solution were added and the pH was adjusted. The mixture was conditioned for 10 minutes. Medical air (breathing grade) was allowed to flow through the cell from a hole in the middle of the cell during this conditioning period to maintain the oxygen concentration in solution at a saturation value of 8.2 ppm. After conditioning, the sample was floated in an air flow of 30 ml/minute for 2 minutes. The samples were xanthated in solutions saturated with medical air.

b. In argon-saturated solution.

The 0.001M depressant solution was purged with pure argon in a 2000 ml flask for 30 minutes prior to use. The argon was previously passed through a bottle of alkaline pyrogallol solution in order to remove traces of oxygen. A two gram xanthated sample was placed into the cell, then argon was allowed to
flow through the cell until the oxygen meter indicated a zero reading. Then 100 ml of the deoxygenated depressant solution was introduced and the pH was adjusted. The mixture was conditioned for 10 minutes. Argon was purged through the cell during conditioning to maintain an oxygen concentration of less than 0.001 ppm, as indicated by the YSI model 54 oxygen meter. After conditioning, the material was floated with 30 ml/minute argon for 2 minutes.

In this series of tests, the samples were previously xanthated in argon-saturated solutions. For comparison purpose, tests were also conducted using samples xanthated in solutions saturated with medical air.

2.3 Determination of Adsorption and Desorption

2.3.1 Thioglycollic Acid (TGA)

The concentration of thioglycollic acid was determined by iodine titration [3][22]. It is believed that TGA is oxidized to its corresponding dimer (DTGA) during titration [22]. The reaction is:

$$2 \text{HSCH}_2\text{COOH} + \text{I}_2 = \text{HOOCCH}_2\text{SSCH}_2\text{COOH} + 2 \text{HI} \quad (3)$$
This indicates that only the concentration of the monomer can be determined by titration. To determine the concentration of TGA solution containing dimer, the solution was first reduced by zinc metal then titrated with iodine [23]. The conditions in which this titration could be performed were determined and are described in APPENDIX II.

2.3.2 Ethyl Xanthate

The concentration of ethyl xanthate was determined by ultraviolet spectroscopy. Measurements were made at the strong xanthate absorption peak of 301 nm using a Perkin-Elmer Model Lambda 3 UV-VIS spectrophotometer. A standard calibration curve was established by measuring the absorbance of a series of ethyl xanthate solutions at their natural pH values. This curve is shown in Fig. 6.

2.3.3 Test Procedure

The adsorption of TGA onto the mineral surface, and the removal of ethyl xanthate from the mineral surface were determined simultaneously. A typical test flowsheet is shown in Fig. 7.

When adsorption and desorption were to be conducted in an inert atmosphere, the stirring was performed in a sealed beaker purged with nitrogen. The solution was previously purged with nitrogen for 30 minutes before the sample was introduced.
Fig. 6  Beer's Law for Potassium Ethyl Xanthate
Using a 1 cm Quartz Cell (at 301 nm)
Xanthated sample

\[50 \text{ ml } 10^{-3} \text{M TGA, adjust pH}\]

Stir

Filtration

20 ml filtrate, titrate directly with 0.005N I\(_2\)

20 ml filtrate, adjust pH to 1, add zinc metal, stir 5 min.

A few ml of filtrate, for UV spectrophotometry

Filtration

Readjust pH to 3.5 - 7, titrate with 0.005N I\(_2\)

Fig. 7 Adsorption/Desorption Test Procedure
2.4 **Zeta Potential Measurements**

To measure the surface charge of mineral treated with reagents, 0.5 gram sample was ground in an agate mortar for two or three minutes then placed in 50 ml reagent solution. After stirring 5 minutes at the required pH value, the supernatant was poured into an electrophoresis cell (thus only the fine particles which were suspended in supernatant went to the cell) to measure the electrophoretic mobility of the colloidal mineral particles. For each sample, ten particles were tracked along one microdivision, and the average microelectrophoretic mobility was calculated.

2.5 **Identification of Reaction Products**

A Perkin-Elmer Model 283B double beam infrared spectrophotometer was used to identify the surface reaction products. Spectra were recorded using both transmittance and reflectance techniques.

2.5.1 **Transmission Spectra**

The conventional KBr pellet method was employed [24]. Samples of chalcopyrite, galena and synthetic zinc sulphide were first ground in a Spex tungsten carbide mill* for one to two hours. Each sample was then placed in a 1000 ml cylinder and allowed to settle for a period of time after

* Model 8000-11, made by Spex Industries Inc. 3880 Park Ave., Metuchen, N.J., USA
which the particles remaining in the supernatant were all calculated to be less than 2.5 microns. No reagents except pH modifiers were added during the sedimentation of the mineral samples. The supernatant was then filtered. The cake was dried and stored in a vacuum desiccator for use in preparing KBr pellets.

To make a KBr pellet, 100 mg of the above sample was reacted with 50 ml 0.01M reagent solution. For galena, the concentration of solution was sometimes 0.001M, which was specified individually. After filtering and drying the sample, a given amount was weighed out (0.5 mg for chalcopyrite and galena, 1 mg for zinc sulphide), mixed with 300 mg KBr in an agate mortar. After 3 minutes of subsequent vacuum evacuation in the die, the mixture was pressed into a transparent pellet at 4800 psi and then subjected to IR identification. The rest of the dry sample was then reacted with the second reagent, and the above procedure repeated.

2.5.2 Attenuated Total Reflectance Spectra

When a beam of radiation encounters an interface between two optically distinct media, a portion of it enters the second medium and a portion is reflected from the surface. If the radiation approaches the interface from the direction of the medium of greater refractive index and the angle of incidence exceeds the critical angle for total internal reflection, the radiation can be totally reflected.
In this situation an evanescent wave is propagated along the direction of the interface. Its extension into the optically rarer medium is damped exponentially and very rapidly, but the wave is exposed to the medium effectively enough to be attenuated according to the absorption coefficient of that medium. If a sample of some material is intimately joined to the surface of an optically denser material, radiation that would otherwise be totally internally reflected at the surface is attenuated by the sample. This is what is called the attenuated total reflection (ATR).

In this experimental work a Harrick versatile reflection attachment was placed in the sample chamber of the infrared spectrophotometer and a zinc sulphide prism was used as a double sampling internal reflection element (see Fig. 8 for the optical system). At an incident angle of 45°, this prism produces 63 internal reflections. In this way, the absorption by a thin film of sample on the prism surface can be intensified. The spectra presented are the difference between the spectra after and the spectra before reagent treatment of the prism. For repeated use, the prism was cleaned in a plasma cleaner* at setting 9 for 4 minutes.†

* Made by Harrick Scientific Corporation, Croton Dam Road, Box 867, Ossining, N.Y. 10562, USA
† Infrared spectra indicated that no organics were present at the ZnS prism surface after treatment in the cleaner at this condition.
Fig. 8 Optical Path of the Multiple Internal Reflection Attachment.
CHAPTER 3
EXPERIMENTAL RESULTS

3.1 Predominant Species in TGA Solution

It has been mentioned that thioglycollic acid has the formula:

\[ \text{HS-CH}_2\text{-COOH}. \]

Both the carboxyl and the mercapto groups possess acidic properties. From the acid-base titration curve of the TGA used in these experiments (Fig. 9), it was observed that TGA underwent only one step dissociation in the pH range tested. The dissociation constant was calculated to be \(2.5 \times 10^{-4}\), using a method described in reference [25]. This suggests that only dissociation of the carboxyl group occurs:

\[ \text{HSCH}_2\text{COOH} = \text{HSCH}_2\text{COO}^- + H^+ \quad (4) \]
\[ K = 2.5 \times 10^{-4} \]

It is known that thioglycollic acid can be oxidized to its corresponding dimer. It has been reported that diluted TGA solution was oxidized rapidly when stored in a clear flask [3]. Test results showed that as long as the flask was well stoppered, the TGA would not be oxidized for a fairly
Fig. 9 Titration Curve of Thioglycollic Acid (TGA)

TGA: 0.01 M, 100 ml

NaOH: 0.102 M
In both iodine and acid-base titrations, the amount of iodine and NaOH consumed was very close to the equivalent amount. This meant that the concentration of TGA determined by acid-base titration was equal to that determined by iodine titration, which indicated that the TGA was relatively pure and free of easily oxidized impurities.

The above results suggested that the predominant species in a stocked TGA solution were pure TGA and its dissociation product thioglycollate. As shown in Fig. 11, above pH 6, TGA was completely dissociated.

### 3.2 Stoichiometry of Thioglycollate Salt Formation

TGA reacts with copper sulphate to form a black precipitate and with lead nitrate to form a light yellow precipitate. In principle, these metal ions could be attached to either the carboxyl group, or the mercapto group, or to both. To determine to which group the metal ions have been attached, a stoichiometric reaction test was conducted. Because of the difficulties in determining the concentration of TGA in the multispecies system (iodine titration technique was used, which is an oxidation-reduction process), a large dosage of metal ions was used against TGA. Tests were conducted at a low pH (approximately 3) and at a high pH (7-9) for both copper and
Fig. 10 Iodine Titration of Stocked Thioglycollic Acid Solution

0.005 N I₂/1 ml 10⁻²M stocked solution

O TGA solutions stored in well-stopped clear flask; Δ TGA solutions stored in a beaker open to air.
Fig. 11  Dissociation of Thioglycollic Acid

Dissociation constant:  $2.51 \times 10^{-4}$

$[R^-]$: concentration of thioglycollate group, $\text{HSCH}_2\text{COO}^-$

$C_0$: original concentration of thioglycollic acid
lead. The results are listed in Table III. As seen, at pH of approximately 3, a large amount of residual metal ions was present in the system, thus it could be assumed that the TGA had been totally consumed. The stoichiometric ratios were very close to 1 at pH 3 for both metal ions. As shown by the Pourbaix diagrams [26] (see Appendix III), under this condition, the metals were present in the system as pure metal ions, it was thus considered that no other reactions than metal-thioglycollate precipitation could occur. This indicates that at this low pH, one metal ion reacts with one TGA molecule to form a precipitate.

Higher consumption of metal ions at high pH values was probably due to the formation of hydroxide as well as thioglycollate (also see Appendix III for the Pourbaix diagrams).

3.3 Depressive Action of TGA on Sulphide Minerals

Hallimond Tube flotation results for chalcopyrite, galena and copper-activated sphalerite, using TGA as depressant, are presented in Figs. 12 to 14. The depressive action was marked on all the sulphide minerals tested. The general observation was that for a given concentration of TGA, there was a narrow pH range in which the sulphide minerals became nonfloatable. They then remained unfloated with an increase in pH. These critical pH values for $10^{-4}$M TGA were, for example, about 9 for chalcopyrite, 8 for
Table III  Stoichiometry of the Reaction Between TGA and Copper or Lead Ions

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Cu$^{++}$</th>
<th>Pb$^{++}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original metal*</td>
<td>2.124x10$^{-3}$</td>
<td>2.008x10$^{-3}$</td>
</tr>
<tr>
<td>pH</td>
<td>3.06</td>
<td>8.94</td>
</tr>
<tr>
<td>Final metal</td>
<td>9.442x10$^{-4}$</td>
<td>3.148x10$^{-6}$</td>
</tr>
<tr>
<td>Reacted metal</td>
<td>1.18x10$^{-3}$</td>
<td>2.12x10$^{-3}$</td>
</tr>
<tr>
<td>Reacted/metal/TGA</td>
<td>1.17</td>
<td>2.10</td>
</tr>
<tr>
<td>Solution redox potential, mv**</td>
<td>+443</td>
<td>+348</td>
</tr>
</tbody>
</table>

* Units for the materials are "moles".

** vs. S.H.E
Fig. 12  Hallimond Tube Flotation of Chalcopryrite Treated with Potassium Ethyl Xanthate and Thioglycollic Acid

chalcopryrite/10^{-4} M KEX: 2g/100ml

- O  no TGA;
- □  10^{-5} M TGA;
- O  10^{-4} M TGA;
- △  10^{-3} M TGA
Fig. 13  Hallimond Tube Flotation of Galena Treated with Potassium Ethyl Xanthate (KEX) and Thioglycollic Acid (TGA)

Galena/10⁻⁴ M KEX: 2g/100ml

- O  no TGA;
- □  10⁻⁵ M TGA;
- △  10⁻⁴ M TGA;
- ▲  10⁻³ M TGA
Fig. 14  Hallimond Tube Flotation of Cu-activated Sphalerite Treated with Potassium Ethyl Xanthate(KEX) and Thioglycollic Acid(TGA)

Sphalerite/10⁻⁴ M KEX: 2g/100ml

○ no TGA; □ 10⁻⁵ M TGA;
○ 10⁻⁴ M TGA; △ 10⁻³ M TGA
Cu-activated sphalerite and 4 for galena. The most marked depression by TGA was observed with galena.

Reversing the order of reagent addition from KEX + TGA to TGA + KEX did not seem to change the depressive action. Figs. 15 and 16 show the test results with chalcopyrite and galena. Both indicate the same depression of minerals.

Ammonium thioglycollate, which has been used in commercial flotation separations, also effectively depressed chalcopyrite (see Fig. 17).

A comparison was made between thioglycollic acid and glycollic acid (GA). As shown in Figs. 18 and 19*, while TGA showed a marked depressive action, GA had no depressive action at all.

3.4 Adsorption of TGA and Removal of Adsorbed Xanthate

In this series of tests, the xanthated sample was conditioned with TGA solution for 5 minutes, then the concentrations of TGA and ethyl xanthate were determined and the corresponding adsorption and desorption calculated. DTGA was not detected with iodine titration in this short period of conditioning, its concentration was thus taken as zero. The results for chalcopyrite, Cu-activated sphalerite and galena are shown in Figs. 20, 21 and 22, respectively.

* Tests with unwashed samples. Chalcopyrite is -150+200 mesh.
Fig. 15 Depression Effect of Thioglycollic Acid on Chalcopyrite

Chalcopyrite/10^{-4} M KEX, 10^{-4} M TGA: 2g/100ml

Flotation: Hallimond Tube

△ Conditioned with KEX, then with TGA
○ Conditioned with TGA, then with KEX
Fig. 16  Depression Effect of Thioglycollic Acid on Galena

Galena/10^{-4} M KEX, 10^{-4} M TGA: 2g/100ml

Flotation: Hallimond Tube

- △ Conditioned with KEX, then with TGA
- ○ Conditioned with TGA, then with KEX
Fig. 17 Depression Effect of Ammonium Thioglycollate on Chalcopyrite

Chalcopyrite/10^{-4} M KEX, 10^{-4} M ATG: 2g/100ml

Flotation: Hallimond Tube
Fig. 18 Depressive action of glycollic acid (GA) and thio-glycollic acid (TGA) on chalcopyrite.
chalcopyrite/10^{-4} M KEX: 2g/100ml
  ▲ \text{10}^{-3}\text{M GA}
  ○ \text{10}^{-3}\text{M TGA}
Depressive action of glycollic acid (GA) and thio-glycollic acid (TGA) on galena.

galena/10^{-4} M KEX: 2g/100ml

- $10^{-4}$ M GA
- $10^{-4}$ M TGA
Fig. 20  Adsorption of Thioglycollic Acid on Chalcopyrite and Corresponding Removal of Adsorbed Potassium Ethyl Xanthate

Chalcopyrite/$10^{-3}$M TGA: 1g/50ml

- □ KEX remaining on surface (no TGA)
- ○ KEX remaining on Surface ($10^{-3}$M TGA)
- △ TGA adsorbed
Fig. 21  Adsorption of Thioglycollic Acid on Cu-activated sphalerite
and Corresponding Removal of Adsorbed Potassium Ethyl Xanthate

Sphalerite/10^{-3} M TGA: 0.5g/50ml

- □  KEX remaining on surface (no TGA)
- ○  KEX remaining on surface (10^{-3} M TGA)
- △  TGA adsorbed on surface
Fig. 22  Adsorption of Thioglycollic Acid on Galena and Corresponding Removal of Adsorbed Potassium Ethyl Xanthate

Galena/$10^{-3}\text{ M TGA}$: 0.8g/50ml

- □  KEX remaining on surface (no TGA)
- ○  KEX remaining on surface ($10^{-3}\text{ M TGA}$)
- △  TGA adsorbed
It seemed that adsorption of TGA on both chalcopyrite and Cu-activated sphalerite had a maximum at around neutral pH; adsorption decreased at both higher and lower pH. The adsorption on galena seemed to be constant at acidic and neutral pH, and fell off in alkaline solutions.

In fact, these differences may not be significant. A straight, horizontal line could be drawn through the data points. Besides, the adsorption was determined by measuring the residual concentration of TGA, which, in turn, was determined by iodine titration. In the iodine titration, the iodine consumed can be more than actually needed at both low and high pH values (APPENDIX II). It is thus easy to see that at these low or high pH values, a higher residual concentration of TGA might be obtained leading therefore to a lower adsorption.

Assuming that each thioglycollate radical occupied $2 \times 10^{-19} \text{ m}^2$ of surface site, the coverage of TGA on the mineral surfaces at neutral pH values would be 12 monolayers for chalcopyrite, 15 monolayers for Cu-activated sphalerite and 6 monolayers for galena. The cross sectional area of $2 \times 10^{-19} \text{ m}^2$ was chosen for the carboxyl group based on similar structures. It was expected that the cross sectional area of mercapto group was less than this value. Thus, even if the TGA molecules adsorbed on the surface took different orientations, the surface area occupied by a single TGA molecule would not exceed $6 \times 10^{-19} \text{ m}^2$. At this maximum value,
the multilayer coverage on the mineral surface was still valid.

Removal of previously adsorbed ethyl xanthate was significant in the presence of TGA, especially at high pH values. Again, the most marked removal of xanthate was observed with galena: at a pH value of around 11 previously adsorbed ethyl xanthate was completely removed; but without TGA, only 30% was removed at this pH value.

3.5 Effect of Oxygen on the Adsorption of TGA

Adsorption tests were conducted with extended conditioning. Mineral samples were conditioned in TGA solution at its natural pH (3.4) for up to 4 hours in both aerated solutions and nitrogen-saturated solutions.

The test results for chalcopyrite, Cu-activated sphalerite and galena are shown from Fig. 23 to Fig. 28. DTGA was detected for all three minerals at both aerated condition and in the inert atmosphere (concentration of oxygen was 0.1 ppm). In the latter case, because the oxygen concentration was low the longer conditioning time allowed for the detection of the DTGA formed.

The total amount of TGA (and/or DTGA) adsorbed in aerated condition was a little more for both chalcopyrite and galena, but remained the same as in the nitrogen atmosphere for Cu-activated sphalerite. The numbers of
Fig. 23 Concentration of Reaction Product as a Function of Contact Time at Aerated Condition

Chalcopryite/10^{-3} M TGA: 1g/50ml

- ○ residual TGA
- △ residual DTGA
- □ TGA(DTGA) adsorbed, mole/g
Fig. 24  Concentration of Reaction Product as a Function of Contact Time Under Nitrogen Atmosphere

Chalcopyrite/$10^{-3}$ M TGA: 1g/50ml

○ residual TGA
△ residual DTGA
□ TGA(DTGA) adsorbed, mole/g
Fig. 25  Concentration of Reaction Product as a Function of Contact Time at Aerated Condition

Galena/10⁻³M TGA:  0.8g/50ml

○ residual TGA
△ residual DTGA
□ TGA(DTGA) adsorbed, mole/g
Fig. 26 Concentration of Reaction Product as a Function of Contact Time Under Nitrogen Atmosphere

Galena/10^{-3}M TGA: 0.8g/50ml

- residual TGA
- residual DTGA
- TGA(DTGA) adsorbed, mole/g
Fig. 27 Concentration of Reaction Product as a Function of Contact Time at Aerated Condition

Sphalerite/10^{-3} M TGA: 1 g/50 ml

○ residual TGA
△ residual DTGA
□ TGA(DTGA) adsorbed, mole/g
Fig. 28  Concentration of Reaction Product as a Function of Contact Time Under Nitrogen Atmosphere

Sphalerite/10^{-3}M TGA: 1g/50ml

○ residual TGA
△ residual DTGA
□ TGA(DTGA) adsorbed, mole/g
equivalent monolayers making up the surface coverage at the mineral surface after 4 hours of conditioning, assuming each thioglycollate radical occupied $2 \times 10^{-19} \text{ m}^2$ of surface sites, were as follows:

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>Galena</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

The amount of TGA adsorbed seemed to reach a maximum value after 60 minutes contact. Further conditioning caused little change. The removal of adsorbed xanthate at this fixed low pH value (3.4) was negligible for all three minerals.

3.6 Zeta Potentials of Minerals

Zeta potentials of chalcopyrite, galena and sphalerite are shown in Figs. 29, 30 and 31, respectively. Each presents the zeta potentials of pure mineral, mineral treated with ethyl xanthate and mineral treated with ethyl xanthate plus TGA in solutions open to air.

The minerals were all negatively charged; this was possibly caused by the previous wash with hydrochloric acid solution. They became more negatively charged upon treatment by the reagents. These observations indicated that the
Fig. 29 Zeta Potentials of Chalcopyrite vs. pH

- △ chalcopyrite washed with HCl and water
- ○ chalcopyrite + $10^{-4}$ M KEX
- / chalcopyrite + $10^{-4}$ M KEX + $10^{-3}$ M TGA
Fig. 30  Zeta Potentials of Galena vs. pH

- \( \triangle \) galena washed with HCl and water
- \( \bigcirc \) galena + 10\(^{-4}\) M KEX
- \( \square \) galena + 10\(^{-4}\) M KEX + 10\(^{-3}\) M TGA
Fig. 31 Zeta Potentials of Sphalerite vs. pH

- △ Cu-activated sphalerite
- ○ Cu-activated sphalerite + $10^{-4}$ M KEX
- □ Cu-activated sphalerite + $10^{-4}$ M KEX + $10^{-3}$ M TGA

Sphalerite was previously treated with Na$_2$S and HCl
adsorption of the thioglycollate group onto the negatively charged surface was through a chemisorption process, at least to the first monolayer.

It was noted that the shapes of zeta potential curves of minerals treated by TGA were very similar to those of the adsorption curves of TGA onto the minerals.

3.7 Solution Redox Potential and Mineral Floatability

Figs. 32 to 34 show the flotation results of chalcopyrite using different depressants, the samples being treated in either aerated solutions, or in an inert atmosphere (including conditioning with xanthate and depressants, and flotation). Figs. 38 to 40 present the flotation results of the three sulphide minerals with TGA as depressant. In this series of tests, the samples were all first conditioned with xanthate in aerated solutions, then conditioned with TGA and floated under an inert atmosphere. It is rather unfortunate that not enough sample was available to do the blank tests (tests in the absence of depressants) for comparison. From the previous test results it can be reasonably stated that the recovery and solution redox potential in the absence of depressant will be all higher than those in the presence of the depressant.

As can be seen, an inert atmosphere significantly improved the depressive action of sodium sulphide, but the
Fig. 32  Effect of pH on the Solution Redox Potential and Corresponding Chalcopyrite Flotation (Thioglycollic Acid as Depressant)

xanthated chalcopyrite/10^{-3} M TGA: 2g/100ml

- ▲ △ potential;  ● ○ recovery
- ▲ ● samples xanthated, conditioned and floated in aerated solutions;  △ ○ samples xanthated, conditioned and floated under Argon atmosphere
Fig. 33 Effect of pH on the Solution Redox Potentials and Corresponding Chalcopyrite Flotation (Potassium Cyanide as Depressant)

xanthated chalcopyrite/10⁻³ M KCN: 2g/100ml

- ▲ potential;
- ○ recovery

▲ △ samples xanthated, conditioned and floated in aerated solutions;
△ ○ samples xanthated, conditioned and floated under Argon atmosphere
Fig. 34  Effect of pH on the Solution Redox Potentials and Corresponding Chalcopyrite Flotation (Sodium Sulphide as Depressant)

xanthated chalcopyrite/10^{-3}M Na_{2}S: 2g/100ml

- △ potential; ◇ ○ recovery
- ▲ samples xanthated, conditioned and floated in aerated solutions;
- △ ○ samples xanthated, conditioned and floated under Argon atmosphere
Fig. 35  Redox Potentials of $10^{-3}$ M Thioglycollic Acid Solutions

- Aerated solutions
- Argon-saturated solutions
Fig. 36 Redox Potentials of $10^{-3}$ M Potassium Cyanide Solutions

- ■ aerated solutions
- □ Argon-saturated solutions
Fig. 37  Redox Potentials of $10^{-3}$ M Sodium Sulphide Solutions

- ▲  Aerated solutions
- △  Argon-saturated solutions
depression by KCN seemed to be unaffected. Thioglycollic acid, on the contrary, showed reduced depressive action under an inert atmosphere. This is most clearly seen from Figs. 38 and 40, which show flotation with all samples xanthated in aerated solutions but conditioned and floated under different atmospheric conditions.

Comparison of Figs. 35 to 37 with Figs. 32 to 34 indicated that the redox potentials of depressant solutions were all decreased upon addition of (xanthated) chalcopyrite. Figs. 39 and 40 indicate that the redox potentials of TGA solutions decreased upon addition of xanthated galena and xanthated sphalerite as well (compare Fig. 39 and Fig. 40 with Fig. 35). Redox potentials of the mineral-containing solutions were further decreased in an inert atmosphere.

One interesting observation was that conditions under which xanthation is carried out had a marked influence on the subsequent flotation depression. Tests with chalcopyrite using TGA as depressant indicated that samples xanthated at aerated condition floated better, even when the subsequent flotation was performed in an inert atmosphere, than samples xanthated at an inert atmosphere and then conditioned and floated at the same atmosphere (see Fig. 41).
Fig. 38  Effect of pH on the Solution Redox Potentials and Corresponding Chalcopyrite Flotation, Thioglycollic Acid as Depressant, All Samples Xanthated in Aerated Solutions

xanthated chalcopyrite/10⁻³ M TGA:  2g/100ml

△ △ potential;  ○ ○ recovery  
△ ● samples conditioned and floated in aerated solutions;  △ ○ samples conditioned and floated in Argon-saturated solutions
Fig. 39 Effect of pH on the Solution Redox Potentials and Corresponding Galena Flotation. Thioglycollic Acid as Depressant, Samples Xanthated in Aerated Solutions

xanthated galena/10^{-3}\text{M TGA:} \quad 2\text{g/100ml}

- ▲ △ potential;  ○ O recovery
- ▲ ● samples conditioned and floated in aerated solutions;  △ ○ samples conditioned and floated in Argon-saturated solutions
Fig. 40  Effect of pH on the Solution Redox Potentials and Corresponding Sphalerite Flotation, Thioglycollic Acid as Depressant, Samples Activated (with copper sulphate) and Xanthated in Aerated solution sphalerite/10^{-3} M TGA: 2g/100ml

Δ △ potential;  ● ○ recovery  
△ ● samples conditioned and floated in aerated solutions;  △ ○ samples conditioned and floated in Argon-saturated solutions
Fig. 41 Effect of Xanthation Condition on Chalcopyrite Flotation

xanthated chalcopyrite/10^{-3} M TGA: 2g/100ml

△ xanthated in aerated solutions
○ xanthated in Argon-saturated solutions

samples conditioned and floated under Argon atmosphere
3.8 Infrared Spectra

The spectra involving sulphide minerals were expanded five times (in the transmission region of 70-100%) in order to make them more indicative. Generally, xanthate showed highly characteristic spectra during adsorption on and desorption from the surfaces; The spectra of minerals treated with TGA were far more difficult to interpret.

The sulphide mineral samples used for making KBr pellets had been exposed to the oxygenated water for several hours (section 2.5.1), so quite possibly they were severely oxidized. Fig. 42 shows the spectra of the sulphide mineral samples, together with those of copper sulphate, lead sulphate and quartz. It seemed that both chalcopyrite and galena were oxidized; they might also contain quartz.

3.8.1 Spectra of Metal Thioglycollates

Spectra were obtained with KBr pellets, which were made by mixing 300 mg KBr with 1 mg of a precipitate formed in CuSO₄ and TGA solutions or with 1 mg of a precipitate formed in Pb(NO₃)₂ and TGA solutions. The spectra, together with reference spectra of TGA, DTGA and deuterized TGA (all obtained by passing infrared light through a capillary film between two sodium chloride window plates), are presented in Fig. 43. As seen, absorption peaks at 1704 cm⁻¹ and 1420 cm⁻¹ in TGA, which represent respectively C=O and C-O stretch vibrations in acid carbonyl (COOH) [27], disappeared
Fig. 42 Infrared Spectra of (a) Chalcopyrite, (b) Galena, (c) CuSO$_4$$\cdot$5H$_2$O, (d) PbSO$_4$, (e) Quartz. ----KBr pellets.
Fig. 43 Infrared spectra of (a) copper thioglycollate (KBr pellet), (b) lead thioglycollate (KBr pellet), (c) TGA (capillary film in NaCl cell), (d) DTGA (capillary film in NaCl cell), (e) deuterized TGA (capillary film in NaCl cell)
from the spectra of copper thioglycollate and lead thioglycollate. These were good indications that the carboxyl group was present in the salt as dissociated anion, COO\(^{-}\), a highly resonance-stabilized structure in which the two carbon-oxygen bonds were identical (section 1.1.4). Consequently, the absorption peaks of C=O and C-O disappeared and those present were the asymmetrical stretching vibration of this COO\(^{-}\) (1572 cm\(^{-1}\) for copper salt and 1531 cm\(^{-1}\) for the lead salt) and the symmetrical stretching vibration of the group at around 1350 cm\(^{-1}\).

It is also noted that the absorption peak of mercapto group S-H at 2567 cm\(^{-1}\) disappeared from the spectra of the salts. This indicated that either the TGA had been oxidized in the salt formation process (see the same figure for the spectrum of DTGA), or the metal ions had replaced the proton bonded to the sulphur. This will be further discussed later.

3.8.2 Spectra of Chalcopyrite

The chalcopyrite sample, when treated with potassium ethyl xanthate showed typical absorption peaks of cuprous ethyl xanthate at 1183, 1117 and 1030 cm\(^{-1}\) [29]. A small absorption peak at 1217 cm\(^{-1}\) might indicate the presence of dixanthogen (see Fig. 44(b)). Subsequent treatment by TGA at pH 6.3 did not remove the absorption peaks but at pH 11.5, the intensities of the CuEtX absorption peaks were reduced significantly (see Fig. 44(d)). This figure also shows
Fig. 44 Infrared spectra of (a) chalcopyrite, and chalcopyrite (b) treated with KEX (pH 6.3), (c) treated with KEX (pH 6.3), then with TGA (pH 6.3), (d) treated with KEX (pH 6.3), then with TGA (pH 11.5). (e) reference spectrum of CuEX + (EX)₂, (f) reference spectrum of copper thioglycollate. ——— KBr pellet
absorption peaks at 1719, 1434 and 1295 cm\(^{-1}\), which indicated the presence of TGA; and absorption peaks at 1561 and 1342 cm\(^{-1}\), which indicated the presence of copper thioglycollate.

The spectrum of pure chalcopyrite treated by TGA showed the absorption peaks of both TGA and copper thioglycollate (see Fig. 45(b)). Subsequent treatment of this TGA-treated chalcopyrite by potassium ethyl xanthate at pH 6.2 caused the appearance of three intensive characteristic absorption peaks of cuprous ethyl xanthate (Fig. 45(c)).

3.8.3 Spectra of Synthetic ZnS

Copper activated synthetic ZnS, when reacted with potassium ethyl xanthate showed absorption peaks at 1193, 1117 and 1031 cm\(^{-1}\), which were typical of cuprous ethyl xanthate. These absorption peaks were not removed at pH 6.3 by TGA but were almost totally removed at pH 11.9 (Fig. 46(d)). Fig. 47 shows that ethyl xanthate adsorbs onto the TGA-treated ZnS surface (pH 7.5). The presence of either TGA or thioglycollate on this ZnS surface was rather difficult to distinguish from the spectra shown in Fig. 47.

3.8.4 Spectra of Galena

Fig. 48 presents spectra of galena treated with reagents of concentration of 0.001M instead of 0.01M. This lower concentration was used because it seemed that among
Fig. 45 Infrared spectra of (a) chalcopyrite, and chalcopyrite (b) treated with TGA (pH 5.2), (c) treated with TGA (pH 5.2), then with KEX (pH 6.2). (d) reference spectrum of copper thioglycollate. (e) reference spectrum of \( \text{CuEX} + (\text{EX})_2 \). ——— KBr pellet
Fig. 46 Infrared Spectra of (a) synthetic ZnS, and Cu-activated synthetic ZnS treated (b) with KEX (pH 6.3), (c) treated with KEX (pH 6.3), then with TGA (pH 6.3), (d) treated with KEX (pH 6.3), then with TGA (pH 11.9). (e) reference spectrum of CuEX + (EX)₂. (f) reference spectrum of copper thioglycollate. **---** KBr pellet.
Fig. 47 Infrared Spectra of (a) synthetic ZnS, and Cu-activated synthetic ZnS treated (b) with TGA (pH 7.5), (c) with TGA (pH 7.5), then with KEX (pH 7.5). (d) reference spectrum of copper thioglycollate. (e) reference spectrum of CuEX + (EX)2. ——— KBr pellet.
Fig. 48 Infrared spectra of (a) galena, and galena (b) treated with KEX (pH 6.6), (c) treated with KEX (pH 6.6), then with TGA (pH 6.6), (d) treated with KEX (pH 6.6), then with TGA (pH 9.8). (e) reference spectrum of lead ethyl xanthate. (f) reference spectrum of lead thioglycollate. ---- KBr pellet
the three sulphide minerals tested, galena was most responsive to both KEX and TGA. Absorption peaks typical of lead ethyl xanthate at 1198, 1108 and 1016 cm$^{-1}$ appeared upon treatment by KEX, and subsequent treatment by TGA almost totally removed these absorption peaks even at pH 6.6. These infrared spectra coincide well with the Hallimond Tube flotation results which showed that galena was totally depressed at very low pH values (see Fig. 13).

Fig. 49(b) presents the spectrum of galena treated with 0.01M TGA solution. As seen, three successive absorption peaks at 1557, 1365 and 1218 cm$^{-1}$ showed clearly the presence of lead thioglycollate (refer to Fig. 49(d)). For this TGA-treated galena sample, when reacted with 0.001M KEX at pH 5.2, lead ethyl xanthate was produced on the surface and the adsorbed lead thioglycollate was significantly removed (Fig. 49(c)). This result, at first sight, did not seem to coincide with the flotation result of galena. Fig. 16 shows that galena was totally depressed at this condition. The reason for the discrepancy was probably that the flotation was performed in the presence of both potassium ethyl xanthate and thioglycollic acid in the solution, whereas the infrared spectrum was recorded using a filtered and dried TGA-treated galena sample so that the thioglycollic acid was absent from the potassium ethyl xanthate solution.
Fig. 49 Infrared spectra of (a) galena, and galena (b) treated with TGA (0.01M, pH 5), (c) treated with TGA (0.01M, pH 5), then with KEX (0.001M, pH 5.2). (d) reference spectrum of lead thioglycollate. (e) reference spectrum of lead ethyl xanthate. --- KBr pellet
3.8.5 Reflectance Spectra

As mentioned previously, reflectance spectra were recorded with an internal reflection element—a ZnS prism. Since this prism absorbed incident infrared light completely in the range 1850 cm\(^{-1}\) to 1650 cm\(^{-1}\), the detection of thioglycollate on the prism surface became very difficult. Spectra were recorded only in the range 1300 to 1000 cm\(^{-1}\), as shown in Fig. 50 and Fig. 51.

Spectra very similar to those of the reference transmission spectra were observed. Absorption peaks typical of cuprous ethyl xanthate at 1197, 1118 and 1032 cm\(^{-1}\) and absorption peaks typical of dixanthogen at 1239 and 1268 cm\(^{-1}\) appeared when the CuSO\(_4\)-treated ZnS prism was placed in 0.001M KEX solution for 4 hours (Fig. 50(a)). These absorption peaks were not significantly removed at pH 6.1 by reacting with 0.001M TGA even after a 4 hour contact, but were removed at pH 11.7.

Fig. 51 shows the adsorption of potassium ethyl xanthate on the TGA treated prism surface. After reaction for one hour, the presence of cuprous ethyl xanthate on the surface became clear and after four hours reaction, dixanthogen is formed on the surface as well as cuprous ethyl xanthate.
(c) ZnS prism activated with copper and contacted with KEX for 4 hours, then reacted for 4 hours with TGA at pH 11.7.

(b) ZnS prism activated with copper and contacted with KEX for 4 hours, then reacted for 4 hours with TGA at pH 6.1.

(a) ZnS prism activated with copper and then reacted with KEX for 4 hours at pH 6.5 (natural pH).

Fig. 50 Infrared Spectra of ZnS Prism Treated with KEX, then with TGA. ---- ATR.
Fig. 51 Infrared Spectra of (a) CuEX + (EX)$_2$ (KBr pellet), and ZnS prism activated by Cu, contacted with TGA for 4 hours and then reacted with KEX for (b) 1 hour, (c) 4 hours at pH 6. --- ATR.
3.8.6 Miscellaneous Spectra

Fig. 52 presents spectra of copper thioglycollate reacted with 0.001M KEX solution. Absorption peaks typical of cuprous ethyl xanthate appeared after 30 minutes contact with the solution but the absorption peak at 1030 cm$^{-1}$ is broader and shifted a little to a lower frequency. Spectra were also recorded with cuprous ethyl xanthate precipitates samples reacted with 0.001M TGA solution, but no change in the spectra was observed even after 60 minutes contact (see Fig. 53).

3.9 Differential Flotation of Synthetic Mineral Mixtures

A wide pH region for possible selective separation was seen in the single mineral flotation of chalcopyrite and galena using TGA as depressant (Fig. 12 and 13). An attempt was then made to separate synthetic mixtures of the same minerals. The flotation separation was performed using a P/S cell at a nitrogen flowrate of 30 ml per minute, with flotation for one minute when the depressant concentration was $10^{-4}$M, and two minutes when it was $10^{-3}$M. The mixed mineral separation results, as shown in Fig. 54 were not so encouraging, however. Similar tests were conducted with potassium cyanide and sodium sulphide as depressants (Fig. 55 and 56). It was observed that only cyanide could make a satisfactory separation, although the pH range at which separation was effected was very narrow (Fig. 55).
Fig. 52 Infrared spectra of (a) copper thioglycollate, and copper thioglycollate treated with 0.001M KEX at pH 6.5 for (b) 10 min. (c) 30 min. (d) 60 min. (e) reference spectrum of CuEX + (EX)₂. ---KBr pellet
Fig. 53 Infrared Spectra of (a) CuEX + (EX)$_2$, (b) CuEX + (EX)$_2$ reacted with 0.001M TGA solution for 60 minutes at pH 3.5. ---- KBr pellet.
Fig. 54 Flotation Separation of Synthetic Chalcopyrite-Galena Mixtures with Thioglycollic Acid

chalcopyrite/galena/10^{-4} M KEX: lg/lg/100ml

- △ recovery of chalcopyrite
- ○ recovery of galena
- ▲ 10^{-4} M TGA;
- △ ○ 10^{-3} M TGA
Fig. 55 Flotation Separation of Synthetic Chalcopyrite-Galena Mixtures with Potassium Cyanide

chalcopyrite/galena/10^{-4}\text{M KEX: } 1g/1g/100ml

\begin{itemize}
  \item $\triangle$ recovery of chalcopyrite
  \item $\bigcirc$ recovery of galena
\end{itemize}

concentration of KCN: $10^{-3}\text{M}$
Fig. 56 Flotation Separation of Synthetic Chalcopyrite-Galena Mixtures with Sodium Sulphide

chalcopyrite/galena/10^{-4}\text{ M KEX: 1g/1g/100ml}

- ▲ 10^{-4}\text{ M Na}_2\text{S;}
- △ 10^{-3}\text{ M Na}_2\text{S}
- △ recovery of chalcopyrite
- ● recovery of galena
Chalcopyrite-sphalerite separations were performed at different levels of sphalerite activation. As seen in Fig. 57, at a fixed pH of 10.5, when there was no activation of sphalerite, the separation was sharp. But the differences in floatabilities diminished rapidly with the increase in the level of copper activation of sphalerite. Figs. 58 and 59 show that with a copper concentration of $10^{-5}$M, fairly good separation could be achieved in a wide range of pH values but with a copper concentration of $2 \times 10^{-4}$M, the separation was not good at all.
Fig. 57  Flotation Separation of Synthetic Mixtures of Chalcopyrite and Cu-activated Sphalerite
chalcopryite/sphalerite/10^{-4} M KEX: 1g/1g/100ml
△ recovery of chalcopryite
○ recovery of activated sphalerite
concentration of TGA: 10^{-5} M
Fig. 58  Flotation Separation of Synthetic Mixtures of Chalcopyrite and Sphalerite Activated with $10^{-5}$ M Copper Sulphate Solution

chalcopyrite/sphalerite/$10^{-4}$ M KEX: 1g/1g/100ml

- Δ recovery of chalcopyrite
- ○ recovery of sphalerite

concentration of TGA: $10^{-5}$ M
Fig. 59 Flotation Separation of Synthetic Mixtures of Chalcopyrite and Sphalerite Activated with 2x10^{-4} M Copper Sulphate

chalcopyrite/sphalerite/10^{-4} M KEX: 1g/1g/100ml

△ recovery of chalcopyrite
〇 recovery of sphalerite

concentration of TGA: 10^{-5} M
4.1 Structure of Thioglycollate Salt

Since both the mercapto group and the carboxyl group of the TGA molecule possess acidic properties and both are chemically reactive, when metal ions are reacted with TGA to form a salt, bonding could occur through either one of the groups, or through both.

It has been seen from Fig. 43 that the absorption peak of the mercapto group disappears from the IR spectra of the copper and lead salts. This indicates that although not dissociated in aqueous solutions, the proton in the mercapto group could have been substituted by metal ions. On the other hand, the spectra of salts indicate the disappearance of the carbonyl group absorption peak, and show the symmetrical and asymmetrical stretching of the resonance-stabilized COO⁻ group. This could be caused by the pure ionized carboxyl group, or by a carboxyl-metal bonding. Kagarise [30] has found that there is a direct relationship between the asymmetrical stretching frequency and the electronegativity of the metal ions bonded to the carboxyl
groups. Since copper and lead ions have different electronegativities (1.9 for copper and 1.8 for lead [31]), and different asymmetrical stretching frequencies have been observed, i.e., 1572 cm\(^{-1}\) for copper thioglycollate and 1531 cm\(^{-1}\) for lead thioglycollate, it can be said that these metal ions have also bonded to carboxyl group.

The stoichiometric reaction tests showed that in an acidic environment in which the metals are present as ions, for every TGA molecule reacted, one metal ion was consumed. Since the metal ions are divalent, in order to maintain the overall neutrality of the solution, the TGA molecule should act as divalent as well. This indicates that the univalent carboxyl group and mercapto group are both participating in the precipitation reactions, which in turn means that the metal ions are likely bonded to both carboxyl and mercapto groups.

In the case of copper thioglycollate, it was observed that slightly more copper ions were consumed than would be indicated by a 1:1 stoichiometry (Table III). This may be due to the fact that TGA is a reducing agent, which, when mixed with copper sulphate, reduces some Cu\(^{2+}\) ions to Cu\(^+\), so that some of the salt was in the form:

\[ \text{CuOOCH}_2\text{CS-Cu-SCH}_2\text{COOCu} \]

and this requires more copper ions to be consumed than the unit stoichiometrical ratio.
4.2 Adsorption Mechanisms of TGA

4.2.1 Depressive-Responsible Species of TGA

It is noted that the floatabilities of sulphide minerals modified by TGA decrease rapidly in a narrow pH range then level off with the increase in pH (section 3.3). If these pH values are taken as critical pH values to prevent the contact between gas bubbles and mineral particles, then the so-called "contact curve" can be drawn. This is shown in Fig. 60. Compared with Fig. 1, the contact curve of sodium sulphide, it is seen that the depressive actions of the two reagents are very similar. Since the actual depressive species in sodium sulphide is SH\(^-\) (section 1.1.2), from this similar behaviour, the mercapto group in TGA molecule is suspected to be the species responsible for the depression.

More convincing evidence is seen from the comparison test between TGA and GA. In section 3.3, it has been shown that unlike TGA, GA has no depressive action on the sulphide minerals. GA has the chemical formula: HOCH\(_2\)COOH. The only difference between the two reagents is that GA has a hydroxyl group attached to the -CH\(_2\)- group whereas TGA has a mercapto group attached to the -CH\(_2\)- group. So the different depressive behaviour is solely determined by the presence or absence of the mercapto group.
Fig. 60 Contact Curve of Thioglycollic Acid

Fig. 61 Schematic Diagram of the Possible Adsorption Model of Thioglycollic Acid onto Sulphide Mineral Surface
4.2.2 Adsorption of TGA

It has been discussed in section 4.1 that metal ions can be bonded to both mercapto and carboxyl groups, which implies that a TGA molecule can be adsorbed onto the sulphide mineral surface through a mercapto group, or through a carboxyl group, or through both.

The TGA molecules adsorbed onto the mineral surface through both of the groups form an "arch" on the mineral surface, exposing the \(-\text{CH}_2-\) group to the surroundings. Since this form of adsorption is not likely to be either strongly hydrophobic nor strongly hydrophilic, it will not significantly affect the floatabilities of sulphide minerals. Furthermore, the formation of subsequent multilayer coverage onto this "arch" is rather unlikely. It thus seems that this form of adsorption does not contribute much to the overall adsorption and depressive action of TGA.

The TGA molecules adsorbed through the carboxyl group will not cause depression in the xanthate solution. Because if they did, glycollic acid, which can also be adsorbed onto the mineral surface through the carboxyl group, would be expected to show a stronger depressive action than thioglycollic acid. This is not the case.

Actually, the carboxyl-group-bonded TGA is displaced by the subsequent treatment with ethyl xanthate, and this is most clearly seen from Fig. 49. Only the
mercapto-group-bonded TGA can be firmly adsorbed on the surface, and displace adsorbed xanthate or compete for surface sites with xanthate.

The adsorption through the carboxyl group or through the mercapto group counts for the first chemisorbed monolayer. Subsequent adsorption onto this layer can be through hydrogen bonding and through -S-S- bonding (dimer formation) due to oxidation (Fig. 61).

It is noted that this adsorption model is different from the one proposed by Raghavan and Unger [3], who suggested a constant coverage of TGA at a chalcocite surface and the DTGA, which was formed by the interaction of aqueous TGA with adsorbed TGA on the surface, went into solution instead of remaining on the surface.

4.3 Effect of Oxygen

The experimental results indicate that a higher oxygen concentration in solution causes more residual DTGA to be produced and enhances the adsorption of TGA and/or DTGA. The production of DTGA is not surprising, but the enhanced adsorption, at first sight, is not so obvious. It is generally thought that the oxidized dimer, DTGA, will be adsorbed only through a physical bonding of some sort, which would not be as strong as a chemisorption. Considering the model proposed in the previous section, in which a
chemisorbed TGA monolayer is covered by TGA molecules through hydrogen bonding and by DTGA molecules through -S-S- bonding, it becomes clear that an oxidative environment, such as a higher oxygen concentration, will enhance the multilayer adsorption of thioglycollic acid due to the facilitated DTGA dimer formation.

This also explains why, unlike sodium sulphide which shows a significantly improved depression in oxygen-deficient condition (Fig. 34), the depressive action of TGA is not reduced by the presence of oxygen but on the contrary, seems to become even more evident (see Fig. 38 and Fig. 40). The interesting result is that this improved depressive action of TGA in air is observed with chalcopyrite and Cu-activated sphalerite, both of which have been shown to produce large amounts of residual DTGA in excess of residual TGA in aerated solutions (see Fig. 23 and Fig. 27).

4.4 Selectivity

Since TGA functions much like hydrosulphide, HS⁻, which is a depressant for almost all sulphide minerals, the selective separation of sulphide minerals using TGA is not promising, as observed in the differential flotation tests. But since it is less toxic than cyanide and less affected by oxidation than sodium sulphide or hydrosulphide, it can be used to replace these reagents in certain situations.
CHAPTER 5
CONCLUSIONS

The environmental control policies and cost considerations, resulting from wasteful consumption of reagents, limit the use of inorganic depressants. As a result, a large variety of organic depressants have recently been developed. Among them, thioglycollic acid, or thioglycollate, has been successfully used in several Cu-Mo flotation plants.

This experimental work was conducted with the aims of developing a basic understanding of the depressive mechanisms of thioglycollic acid, and searching for potential uses of this reagent as a selective depressant. This work has resulted in the following conclusions:

a. Thioglycollic acid shows strong depressive action on the sulphide minerals* tested, with the most marked effect on galena.

b. When ethylxanthate-treated sulphide minerals are

* In this section, "sulphide minerals" refer to chalcopyrite, galena and Cu-activated sphalerite.
subject to treatment by thioglycollic acid in an alkaline solution, the adsorbed ethylxanthate is desorbed.

c. Thioglycollic acid exhibits multilayer coverage on the sulphide minerals (assuming that each TGA radical occupies $2 \times 10^{-19}$ to $6 \times 10^{-19}$ m$^2$ of surface site). The adsorbed species are a mixture of metal thioglycollate in the form of $\text{MSCH}_2\text{COO}^-$ and $\text{HSCH}_2\text{COOM}$, thioglycollic and dithiodiglycollic acids.

d. Ethyl xanthate can adsorb on TGA-treated sulphide mineral surfaces and on metal thioglycollate precipitates by displacing $\text{MeOOC}^-$ groups around neutral pH.

e. The depressive action of thioglycollic acid is not reduced by the presence of oxygen. In fact, oxygen helps the precipitation of thioglycollic acid onto mineral surface in the form of dithiodiglycollic acid, improving the depression.

f. The depressive action of thioglycollic acid resembles that of hydrosulphide, which is a depressant for almost all sulphides. Selective separation of sulphide minerals by TGA alone is then rather difficult, at least under the conditions used in this study. This reagent can be a good substitute
for cyanide and sodium sulphide only in some circumstances.
REFERENCE


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APPENDIX I

Kodak Irtran II Material
PRODUCTION OF KODAK IRTRAN MATERIALS

IRTRAN Materials are classed as hot-pressed polycrystalline compacts. Each is made from well-known pure inorganic chemical compounds: IRTRAN 1 Material is magnesium fluoride (MgF$_2$) and IRTRAN 2 Material is zinc sulfide (ZnS).

Each compound of IRTRAN Materials is refined to a pure powder state prior to hot-pressing into an optical blank. Purity is equal to, or better than, the same material of a CP (chemically pure) grade.

Each IRTRAN Material starts in a fairly conventional round mold where the temperature is raised by inductive heating and extreme pressure is applied through means of a hydraulic press. A schematic of the mold and pressing arrangement is shown in Figure 5.

Enough powder is loaded in each mold to form a final densified blank of what is called "optical density." The powder or "charge" is never heated high enough to melt to a truly fluid mass. Plastic deformation is considered the primary mechanism of densification. Final density is extremely close to theoretical density. There is no evidence of any measurable porosity. While the mass is composed of many tiny crystalline aggregates, each grain face is so closely packed against adjacent grain faces that optical transmittance is possible. However, this grain "nesting" does not become 100 percent complete, accounting for the visual scattering evident in IRTRAN Materials. Examples and comparisons of visual transmittance scattering can be noted in Figure 6. Further reference to scattering also can be noted on page 16.

The combined requirements of a containment mold and high molding pressures tend to define the maximum sizes that can be offered readily and economically in IRTRAN Materials. Available sizes of circular blanks and spherical domes or caps are tabulated in Table 1.

Most IRTRAN Materials emerge from the presses and molds as circular flat blanks. The first test to determine blank quality is a transmittance test which must be made through buffed spots on each face of the blank. After a blank meets with initial acceptance, it is then sent to our optical shop for slicing. Here, rough wafers larger than listed stock thicknesses are cut from the entire blank diameter and are then ground and face-polished to within tolerances established for each standard thickness. At this point, a complete transmittance check can be made of each slice, after which it is moved to our stock shelves. Polished windows in many sizes are eventually produced.
Index of refraction values were experimentally determined at selected wavelengths between 1 and 10 μ. Coefficients of an interpolation formula were established and reduced by least squares methods, and the values computed. All values beyond 10 μ are extrapolated.

Table A1

Indices of Refraction for INTRAN Materials
Base Index and Coefficients

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Table A2

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APPENDIX II

Conditions of Iodine titration of TGA
Iodine titration of TGA is an oxidation process, so only the unoxidized species are determined. To determine the concentration of TGA with oxidized product, DTGA, the solution is first reduced with zinc metal then titrated with iodine.

1. Determination of reduction time with Zn

To determine the reduction time of TGA solutions with zinc metal, an oxidized TGA solution was prepared by reacting 4 grams of -150# chalcopyrite with 400 ml 0.001M TGA, filtering the solution and leaving it open to air overnight.

The next day, the pH value of the solution was adjusted to 1, zinc metal was added and the solution was stirred for a certain time. After filtration and washing with HCl solution (pH=1), the filtrate was titrated with 0.006N iodine. The results are shown in Fig. A2. It is seen that a reduction time of 5 min. is enough to reduce all the DTGA. It is also noted that the amount of iodine consumed is more than the equivalent amount. This was considered to be the effect of the pH value at which the titration was conducted. Next, the effect of pH on the titration was tested.
Fig. A2  Reduction of Thioglycollic Acid with Zinc Metal and Corresponding Iodine Consumption

$0.006 \text{ N } I_2 / 10 \text{ ml } 10^{-3} \text{M TGA}$
2. Determination of titration pH

A stocked TGA solution was directly titrated with 0.005N iodine at different pH values. Results are shown in Fig. A3. It is seen that only in the pH range of 3 to 9 is the titration result correct.

Since, at pH above 3, the reduction of TGA by Zn was found to be ineffective, the titration procedure was determined to be the Zn-reduction of the solution at pH 1, followed by the titration of the solution at pH 3.5-7.
Fig. A3  Effect of pH Value of TGA Solution on Iodine Titration

0.005 N I₂/ 10 ml 10⁻³ M TGA
APPENDIX III

Pourbaix Diagrams of the Copper-Water System and the Lead-Water System
Fig. A4 Potential-pH Diagram of the Water-Copper System [26]
Fig. A5 Potential–pH Diagram of the Water–Lead System [26]